

UMASS/AMHERST



312066 0015 5691 6

Some Condensation Products
OF
Fluorenone-5-Carboxylic Acid

BY
ROLAND BARNES FRENCH

PHYS
SCI
LD
3234
M268
1922
F875

SOME CONDENSATION PRODUCTS

of

FLUORENONE - 5 - CARBOXYLIC ACID

Rowland Barnes French

Thesis submitted for

the degree of

Master of Science

MASSACHUSETTS AGRICULTURAL COLLEGE

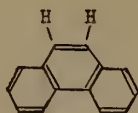
May 1922

PURPOSE OF THE INVESTIGATION

This investigation, the history of which follows, was undertaken with the idea in mind of preparing from diphenic anhydride - which would be obtained from phenanthrene, a byproduct of the coal tar industry - products which would correspond to the phthaleins obtained when phthalic acid is condensed with the phenols. It was felt that a comparison of these two similar series of compounds might present facts which would be of interest. The problem was suggested by Dr. Joseph S. Chamberlain, Professor of Organic Chemistry, Massachusetts Agricultural College.

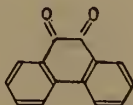
REVIEW OF THE LITERATURE

Phenanthrene (1) is an isomer of anthracene. It is a hydrocarbon which consists of three condensed benzene nuclei, and which has the empirical formula $C_{14}H_{10}$. It is found associated with anthracene in the coal tar distillate which boils above 270° . Its constitution (2) has been proven by the synthesis from stilbene and di-tolyl.



Phenanthrene

When phenanthrene (3) is attacked by an oxidizing agent such as a mixture of potassium bichromate and sulphuric acid the two hydrogens of the central benzene ring are oxidized. A quinone, called phenanthraquinone, is formed which possesses the formula $C_{14}H_8O_2$.



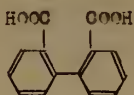
Phenanthraquinone

Phenanthraquinone is usually obtained from commercial phenanthrene which contains, as a rule, ten to twenty percent tarry materials, and anthracene. These impurities (4) are readily gotten rid of since phenanthraquinone, like most quinones, forms a soluble bisulphite addition product.

Phenanthraquinone upon further oxidation forms a compound which is known as diphenic acid. The intermediate nucleus of phenanthraquinone breaks during this oxidation and the two

- (1) Molinari, Organic Chemistry p. 618
- (2) Chamberlain, Organic Chemistry p. 807
Annalen, 196 : 24
- (3) Beilstein vol. III p. 440
- (4) J.A.C.S., vol. 43: p.208

ketone groups become carboxyls. This compound in older



Diphenic acid

references is often spoken of as o- o- bibenzoic acid. The reason for this is apparent because diphenic acid is simply two benzoic acid groups joined together, with the elimination of two atoms of hydrogen, in the positions ortho to the two carboxyl groups.

Several methods have been worked out for the breaking of the bond between the two C-O groups. In Beilstein (1) directions are given, which continue the oxidation of phenanthraquinone with a mixture of potassium bichromate and sulphuric acid similar to the one that was used for the oxidation of phenanthrene. This method, however, is rather cumbersome for it requires not only much oxidizing material, but also considerable time for its satisfactory performance. A.R. van Linge (2) used an alkaline solution of potassium hypobromite to oxidize certain aldehydes and quinones among which was phenanthraquinone. He succeeded in obtaining very high percentage yields of diphenic acid.

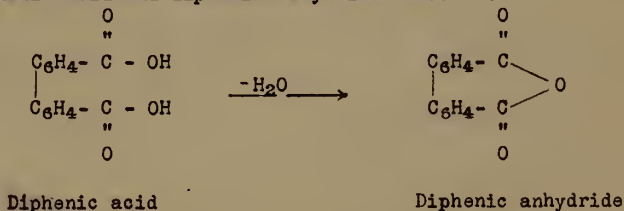
An older method for this oxidation (3) consists of boiling phenanthraquinone with an alcoholic solution of caustic potash. Diphenic acid, however, does not result directly from this treatment until several intermediate reactions have been completed. Benrath and von Meyer (4) in reviewing the work of Klingerschen

- (1) Beilstein: Vol. III p. 1803
- (2) A.R. van Linge : Rec. Trav. Chem 1897, 161 :44-56
- (3) Meyer and Spengler : Ber. 38 :440-450
- (4) Benrath and von Meyer : Ber. 45 : 2707

found that when a mixture of benzene hydrocarbons and various quinones, or diketones, was exposed to the action of the sunlight, reactions took place which resulted in the formation of the ether either of the hydroquinone or of the quinhydrone. So they exposed mixtures of phenanthraquinone and benzene hydrocarbons to the sunlight to see what would happen. They obtained from these mixtures diphenic acid in almost quantitative yield.

Diphenic acid when treated with methyl and ethyl alcohol in the presence of hydrochloric acid (1) forms esters that are called diphenates. Schmidt and Kämpff (2) in working on the substitution products of diphenic acid obtained by the action of nitric acid a p.p. dinitrodiphenic acid which reacted easily with phosphorus pentachloride to form an acid chloride.

When diphenic acid was treated with acetyl chloride in the cold or warmed with acetic anhydride to 130° Anschütz according to Graebe and Aubin (3), found that a molecule of water was eliminated from a molecule of diphenic acid and diphenic anhydride resulted.

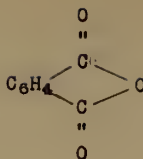
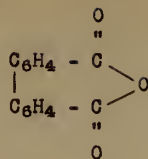


Graebe and Aubin (4) heated diphenic acid with both phosphorus pentachloride and phosphorus trichloride and obtained mixtures of compounds of which diphenic anhydride was one.

Graebe and Mensching (5) recognizing the relationships that existed between phthalic anhydride and diphenic anhydride in structure, tried to obtain material for a comparison of their

- (1) Graebe and Aubin J.C.S. abs., 56 :145
- (2) Schmidt and Kämpff : Ber., 36: 3744
- (3) Graebe and Aubin : Ann. 247:268
- (4) Graebe and Aubin : Ann. 247:268
- (5) Graebe and Mensching, Ber. 13 (1) :1302

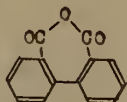
behavior.



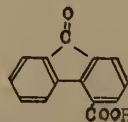
Diphenic anhydride

Phthalic anhydride

First (1) they tried to find the chloride of diphenic anhydride that would correspond to the unsymmetrical chloride of phthalic anhydride. But, material for a comparison could not be obtained here, since by the influence of the chlorides of phosphorus, under one set of conditions, an intramolecular change in the constitution of diphenic anhydride occurred which resulted in the formation of fluorenone -5- carboxylic acid, or *o*-diphenylene-ketone-monocarboxylic acid as it is usually spoken of in earlier references; under different conditions (2)



Diphenic anhydride



Fluorenone -5- carboxylic acid

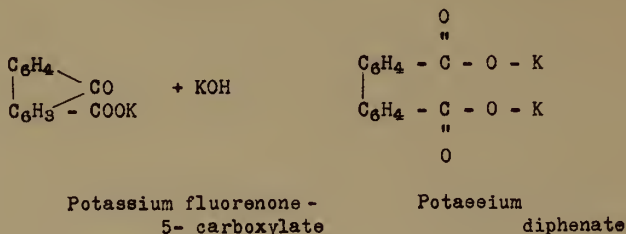
a dichloride of a double molecule of diphenic anhydride was obtained, the constitution of which was doubtful.

Graebe and Aubin worked out several methods for the formation of fluorenone -5- carboxylic acid from diphenic acid and from diphenic anhydride. (a) When diphenic acid (3) was moderately warmed with sulphuric acid a molecule of water was lost and fluorenone -5- carboxylic acid resulted. (b) If diphenic acid (4) was heated with an excess of phosphorus

- (1) Ibid
- (2) Graebe and Aubin, Ann. 247 : 268
- (3) Ibid
- (4) Ibid

oxychloride to the boiling point of the latter, the chloride of the ketone acid was obtained. (c) When either diphenic acid or diphenic anhydride was strongly heated with zinc chloride (1) the ketone acid was obtained. (d) By heating diphenic anhydride to 100° with sulphuric acid (2) the ketone acid resulted.

Graebe (3) also fused fluorenone -5- carboxylic acid with potassium hydroxide and obtained the potassium salt of diphenic acid.



Likewise, (4) by boiling the ketone acid with methyl and ethyl alcohol, in the presence of hydrochloric acid, he obtained the methyl and ethyl esters respectively.

Götz described (5) a method for preparing a condensation product of fluorenone -5- carboxylic acid and benzene by using aluminium chloride as a catalyser. The substances that Graebe and Mensching mentioned (6) as phthaleine or diphenic anhydride with phenol and resorcinol were later found to be (7) condensation products of fluorenone -5- carboxylic acid with the phenols.

- (1) Ibid
- (2) Graebe and Aubin, Ber. 1887 : 846
- (3) Ibid
- (4) Graebe and Aubin, Ber., 1881 1849
- (5) Rudolf Götz : J.C.S. Abt., V 82: 372
- (6) Graebe and Mensching, Ber., 13 (1) : 1304
- (7) Graebe and Aubin, Ber., 1887 : 847

EXPERIMENTAL DATA

The phenanthrene that was used in this investigation was obtained from the Eastman Kodak Company's laboratories. This phenanthrene, which was almost white in color and in the form of a powder, was ninety percent pure. Another lot of phenanthrene that was obtained from the same source was very much darker in color and was only eighty percent pure. The results obtained from the employment of these two different lots of this compound parallel each other, although procedure methods vary a bit. More will be said of this a little later.

Preparation of Phenanthraquinone. The phenanthrene was first oxidized to phenanthraquinone by the procedure given in Beilstein (1). Fifty grams of phenanthrene were weighed and powdered. An oxidizing mixture consisting of two hundred grams of potassium bichromate, three hundred grams of sulphuric acid, and five hundred cubic centimeters of water, was stirred up in a two liter evaporating dish. The phenanthrene was added slowly, with continuous stirring, to this mixture which was afterwards heated to one hundred degrees. As the oxidation was strongly exothermic and apt to go rapidly when heated, care had to be taken to prevent any loss of material thru foaming. After the vigorous action had been completed, a liter of cold water was added to the material in the evaporating dish to reduce the solubility of the phenanthraquinone that had been formed. Upon cooling, the phenanthraquinone was filtered off thru glasswool and washed with water until the washings came thru colorless.

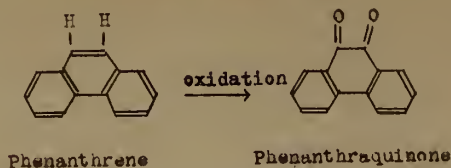
(1) Beilstein, vol. III p. 440.

Purification of Phenanthraquinone. This crude product weighed forty-seven grams. It was purified by suspending the yellowish mass, which contained the phenanthraquinone, in five hundred cubic centimeters of sulphuric acid to remove tarry materials and other acid-soluble impurities; then, after the addition of a liter of water it was washed well with a saturated solution of sodium carbonate to dissolve any diphenic acid which had been formed by the oxidation of the phenanthraquinone. After washing again with water, and finally with ether, to get rid of unoxidized hydrocarbons, the residue contained phenanthraquinone and anthraquinone. These were separated by suspension in two liters of a saturated solution of sodium acid sulphite in which the phenanthraquinone is soluble. (The sodium acid sulphite (1) was made by running sulphur dioxide gas into a solution of sodium carbonate.) The undissolved anthraquinone was filtered off and discarded. The filtrate, which contained the phenanthraquinone in solution, was acidified with an equal volume of dilute sulphuric acid in which were dissolved about fifty grams of potassium bichromate per liter. The finely divided yellow precipitate resulting was filtered off and washed well with water.

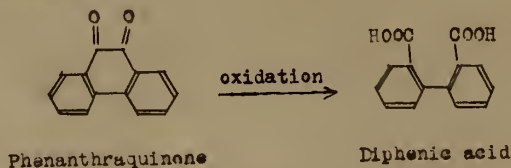
The phenanthraquinone thus obtained gave, on recrystallization from carbon tetrachloride, a fluffy orange-colored, crystalline powder which melted at 202° . It distilled unchanged (360°), was barely soluble in water, slightly soluble in alcohol and ether, and easily soluble in acetic acid, and sulphuric acid with a dark green color.

(1) Gmelin Krant, 2,1 : 320

The reaction involved is as follows.



The next step in the investigation was to obtain diphenic acid by the further oxidation of phenanthraquinone. The following reaction takes place:



Preparation of Diphenic Acid. The method below was outlined in Beilstein (1), but modifications were introduced in some of the details.

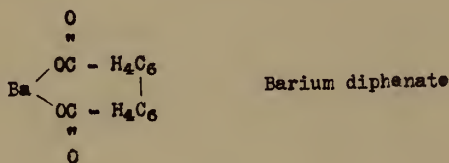
Fifty grams of crude moist phenanthraquinone were stirred into an oxidizing mixture, which consisted of two hundred grams of potassium bichromate, three hundred grams of concentrated sulphuric acid and five hundred cubic centimeters of water. This mixture was placed in a liter round bottom flask on a sand bath under a reflux condenser and heated for two hours moderately, in order not to hasten the reaction too much, as too rapid oxidation causes much inconvenience from foaming. Then, the temperature of the oxidizing bath was raised to one hundred degrees and kept there for six hours. After the addition of one half a

(1) Beilstein, vol. III p. 1803

liter of cold water the mixture was filtered on a Buchner funnel and washed until the washings came thru colorless. After filtration the finely-divided yellow residue was suspended in a liter of a saturated solution of sodium carbonate in which the diphenic acid readily dissolved with the formation of the soluble sodium salt. The insoluble residue, which consisted mainly of unoxidized anthraquinone, was filtered off, and the filtrate was acidified with concentrated hydrochloric acid. Since diphenic acid is insoluble in acid solution the instant that the neutral point was passed a finely-divided white precipitate came down, which was the compound sought. The observation was made that it was much more convenient to turn the diphenic acid solution into the concentrated hydrochloric acid since such a manipulation did away with excessive foaming such as was caused by the reverse process. This precipitate was filtered and well washed with water, in which diphenic acid is only slightly soluble, until the washings were chlorine free. After the precipitated diphenic acid was dried, its melting point was determined and found to be $227^{\circ} - 228^{\circ}$. This constant agreed with the melting point given in the literature. Diphenic acid was found to be a white crystalline powder which was soluble in alkalis, carbonates, and alcohol and only slightly soluble in benzene. Recrystallized from alcohol it formed small needles. The amount of diphenic acid obtained was twenty-seven grams, or approximately a fifty percent yield.

In the preceding oxidation the phenanthrene used was supposedly eighty percent pure. Subsequent oxidations were performed on a product that was labeled ninety percent pure phenanthrene. A satisfactory oxidation of this product required a more powerful agent than was required for

the eighty percent material. This was shown by the fact that when the same amount of oxidizing mixture was used with these two lots of phenanthrene, it was found that the ninety percent phenanthrene was incompletely oxidized and yielded a yellow crystalline product, which did not have a sharp melting point, and which was converted into pure diphenic acid by further oxidation. On this account the ninety percent phenanthrene was oxidized by means of a mixture that contained about twentyfive percent more sulphuric acid and potassium bichromate than was used above; the ratio between the acid and bichromate remaining the same. The diphenic acid obtained when the stronger oxidizing mixture was used had the usual melting point of $227^{\circ} - 228^{\circ}$. A barium salt determination gave a result which agreed with the formula



Percent barium found = 40.45%

Percent barium cal. = 40.72% Difference = .27%

The yield of diphenic acid from this experiment was about fifty percent, practically the same result as was obtained in the preceding oxidation.

In trying to increase the yield of diphenic acid and also in trying to increase the speed of the reaction an oxygen carrier or catalyst, ferrous chloride, was added to the chromic acid mixture which contained the phenanthraquinone. One gram of ferrous chloride was added for

every ten grams of phenanthraquinone used. In this experiment the length of heating the oxidizing mixture was reduced from eight hours to four hours. At the end of this time the diphenic acid was extracted and precipitated as in the preceding oxidation. When the percent yield of diphenic acid from this experiment was calculated, it was found to be sixty percent. This is an increase of ten percent over the yield in the preceding experiment. Subsequent oxidations confirmed these results. Thus it is evident that the presence of ferrous chloride in the oxidizing mixture acted as a catalyser to increase, not only the speed but also the yield of the reaction. The calculation of the percent yields obtained in these experiments was made from the direct ratio of the diphenic acid obtained, to the phenanthrene used.

Since this method for obtaining diphenic acid was obviously cumbersome other processes, which might be more satisfactory, were tried. The next five experiments give the details of this search.

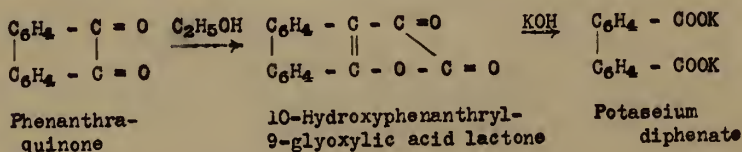
Phenanthraquinone was heated in glacial acetic acid to which barium dioxide was added as an oxidizing agent. Upon saturation of the solution with sodium chloride, after the completion of the oxidation, a precipitate came down which was dissolved in sodium carbonate and precipitated with hydrochloric acid. A twenty percent yield was obtained of a crystalline product which melted at 220° - 221° , but which yielded diphenic anhydride on subsequent treatment (see below.)

Another method that did not give satisfactory results was an attempt to oxidize phenanthraquinone with chromic oxide, with acetic acid employed as a solvent. A little diphenic acid, which made only a small percent yield was obtained. In another experiment in which a mixture of potassium permanganate and sulphuric acid was used as the source of

oxygen, the result was practically the same.

The rather interesting method for the preparation of diphenic acid, that was suggested by Meyer and Spengler (1), was next tried. Twenty-five grams of phenanthraquinone were heated with a ten percent solution of alcoholic potash under a reflux condenser for a week. A yellow crystalline substance was obtained, the melting point of which was $220^{\circ} - 221^{\circ}$. This meltingpoint corresponded to the melting point of the lactone of 10-hydroxyphenanthryl - 9-glyoxylic acid which may be obtained in this way.

The same compound could be obtained by heating glycolic acid with phenanthraquinone in a ethyl alcohol solution. This compound on much longer boiling with the potassium hydroxide was converted into diphenic acid. Ethyl alcohol was a necessary factor for the success of this reaction inasmuch as no such change from phenanthraquinone to diphenic acid took place when methyl alcohol was used as a solvent. Also, it is highly probable that in the above cases of oxidation where acetic acid was used as a solvent, this lactone was obtained (see above.)



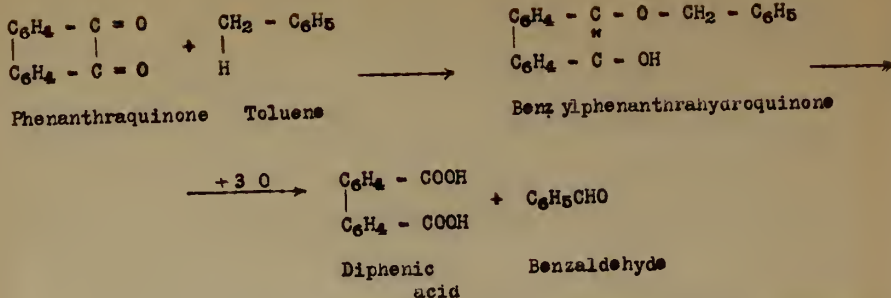
The autooxidation of phenanthraquinone that Benrath and von Meyer described (2) was next attempted. Five grams of phenanthraquinone were put in a large round bottomed flask which contained thirty grams of

(1) Meyer and Spengler, Ber: 38:440 - 450

(2) Benrath and von Meyer, Ber: 45:2707

commercial xylene. The flask and its contents were then exposed to the rays of the sun. After the lapse of several days small crystals, which clung to the sides of the flask, were observed. These crystals were removed, dried, washed with benzene, and recrystallized from water. Only a small amount of the product was obtained, but its physical characteristics corresponded to those of diphenic acid. The same process was repeated, except that toluene was used in the place of xylene, with another lot of phenanthraquinone. The crystals formed in the same manner as above, but by the addition of petroleum ether to the toluene filtrate a small amount of soluble diphenic acid was precipitated. Both the toluene and the xylene filtrates had the odor of aldehyde. The aldehydes were present, however, in such small quantities that they could not be isolated.

The following explanation of the facts of this reaction has been given. It was originally thought that the hydrocarbon was first oxidized to the aldehyde by the oxygen of the air in the presence of sunlight, and that the water resulting made possible the subsequent oxidation of the phenanthraquinone. But it was found that no change in phenanthraquinone occurred when it was suspended in water and exposed to the action of the sunlight. It was therefore assumed that the hydrocarbons added on to the phenanthraquinone yielding a phenanthrahydroquinone ether which thereupon became oxidized in the presence of sunlight yielding diphenic acid and the aldehyde of the hydrocarbon used. The reactions may be represented as follows:



Of the preceding methods described for the oxidation of phenanthraquinone, only one resulted in a considerable yield of diphenic acid, namely that experiment in which a mixture of potassium bichromate and sulphuric acid was used for the oxidation. The next process gave even more satisfactory results.

It was stated in an article by A. R. van Linge (1) that phenanthraquinone might be oxidized to diphenic acid by the action of an alkaline solution of potassium hypobromite. So fifteen grams of phenanthraquinone were placed in a flask together with sixty cubic centimeters of a thirty percent solution of potassium hydroxide to which twenty grams of bromine had been added. This mixture was put on the water bath and heated for two hours. At the expiration of that time the phenanthraquinone had completely disappeared and was present in the flask as the soluble potassium salt of diphenic acid. Upon cooling, and acidifying this solution with hydrochloric acid a voluminous white precipitate was thrown down, which, after being thoroughly washed with water and dried, gave a melting point that coincided with that of diphenic acid (227° - 228°.) The amount of diphenic acid obtained was fifteen grams, a yield that was calculated to be ninety percent. This oxidation by hypobromous acid, altho of not so much theoretical interest as some of

(1) A. R. van Linge, Rec. Trav. Chim. 1897, 161 : 44

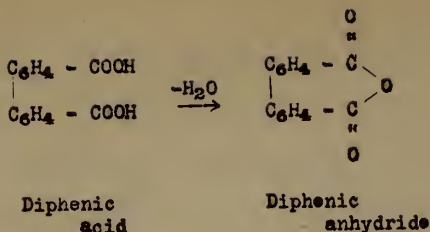
the others described, was by far the most efficient, when considered from the points of both the yield obtained, and the time employed.

Preparation of Diphenic Anhydride. The anhydride of diphenic acid is readily formed by the action of certain dehydrating agents on the acid. The reason for this is apparent since diphenic acid contains two carboxylic groups which are placed adjacent to each other, and which are therefore ideally situated for the facile elimination of a molecule of water between them, with the resulting formation of an anhydride.

Anschütz (1) gave a method for this anhydride formation that was slightly modified by recent work given in an article in the Journal of the American Chemical Society (2). The details of the experiment follow. Twenty-five grams of diphenic acid were weighed out and put in a round bottom flask which contained ^{cubic} seventy-five/centimeters (three times the weight of the diphenic acid) of acetic anhydride. This mixture was heated up to 100° under a reflux condenser for one hour. During the heating a few needle crystals appeared in the flask. The flask was removed from the flame and cooled. The contents of the flask became a solid mass of crystals, which were transferred to a suction filter and washed, first with acetic acid, and finally with ether. After the white needle crystals were sucked dry, a melting point determination made upon them gave 217° as the point of fusion. This agreed with the result cited in the literature.

(1) Graebe and Aubin, Ann., 247 : 268

(2) J.A. C.S., vol. 43 : 208



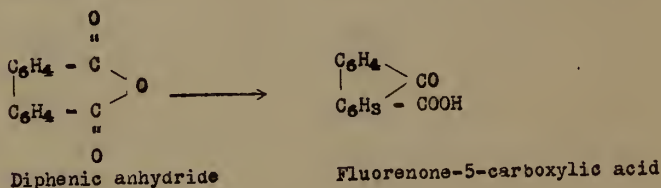
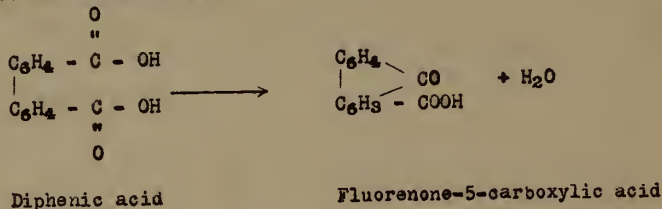
Both diphenic acid and diphenic anhydride when heated with sulphuric acid, or fused with zinc chloride undergo an intramolecular change yielding a compound that is known as o-diphenylene-ketonecarboxylic acid, or fluorenone-5-carboxylic acid. The outline of the following experiments on the formation of fluorenone-5-carboxylic acid was given by Graebe and Aubin in the Annalen. (1)

Preparation of Fluorenone-5-carboxylic acid. Ten grams of diphenic anhydride were warmed to one hundred degrees with thirty cubic centimeters of concentrated sulphuric acid. The diphenic anhydride dissolved to form a compound that gave a deep red color to the solution. When, after cooling, this deep red solution was turned into cold water a voluminous yellow precipitate was formed which was filtered off, washed well with water, and dried. It gave a melting point of 227° - 228° which was the melting point of the ketone acid.

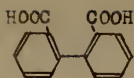
Ten grams of diphenic anhydride were melted with five grams of fused zinc chloride in an iron crucible on an oil bath. The fusion mixture was kept at 200° for an hour. At the expiration of that time the crucible was removed from the bath and allowed to cool. The solid mass that had formed was chipped out of the crucible and heated with water which was slightly acidulated with hydrochloric acid. The zinc chloride

(1) Graebe and Aubin, Ann. 247 : 268

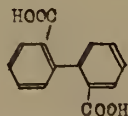
went into solution and was filtered off. The residue was dissolved in a solution of sodium carbonate. From one part of the resulting solution, upon evaporation, yellow needle crystals of the sodium salt of the ketone acid were obtained. The rest of the solution was acidified with hydrochloric acid; the resulting precipitate was filtered off, washed with water until all the chlorides were removed, and dried. This crystalline precipitate gave a melting point of 227° which agreed with the melting point of the ketone acid. It crystallized from alcohol in golden-colored needles and was soluble in sulphuric acid with the formation of the characteristic red color of the ketone acid.



The formation of the ketone acid from diphenic anhydride, as described in the above experiments, would suggest that the course of the reaction, when the ketone acid was formed from diphenic acid, would be from diphenic acid thru diphenic anhydride to fluorenone-5-carboxylic acid. This is, however, not the case, as Graebe points out. Diphenic acid is usually considered to have the structural formula:



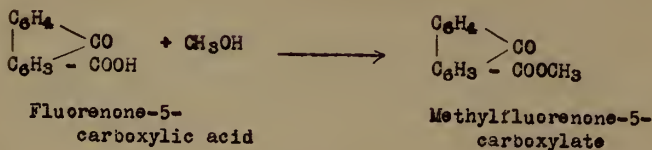
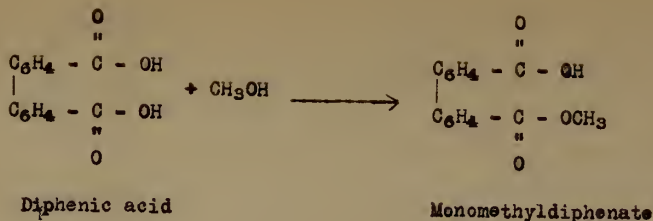
The position of the carboxyl groups being determined by the manner in which diphenic acid is formed by oxidation from phenanthraquinone in which the two quinone groups are adjacent to each other; and also by the way in which diphenic anhydride is built up from diphenic acid. However, the formation of fluorenone-5-carboxylic acid indicates that the formula for diphenic acid may be as follows:



In this formula the carboxyl groups, on a plane surface, appear to be placed opposite, and not adjacent to each other as in the first formula. Whether these two compounds are identical is not known.

Fluorenone-5-carboxylic acid is insoluble in water, easily soluble in hot sulphuric acid and alcohol, but only slightly soluble in ether.

The methyl and ethyl esters of diphenic acid and of the ketone acid were formed by heating the acids, respectively, with methyl and ethyl alcohols, to which a little hydrochloric acid had been added. Upon evaporation the esters were deposited in the form of crystalline cubes.

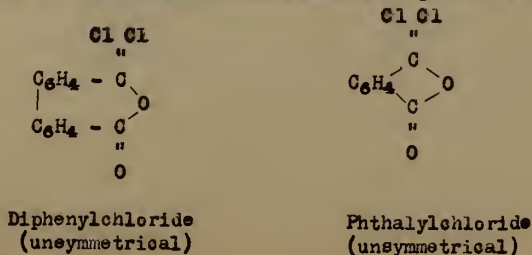


The monomethyldiphenate melted at 110° ; the monoethyldiphenate at 88° . The methyl ester of fluorenone-5-carboxylic melted at 132° , the ethyl ester at 103° . This formation of the methyl and ethyl esters gives a means for the identification of diphenic acid and of the ketone acid; for while the melting points of the two acids coincide, $227^\circ - 228^\circ$, the melting points of their esters are quite different.

Melting Point Determinations.

	Free acid	Methyl ester	Ethyl ester
Diphenic acid	227°	110°	88°
Fluorenone-5-carboxylic acid	227°	132°	103°

The Unsymmetrical Chloride of Diphenic Anhydride. Attempts were made to form the unsymmetrical chloride of diphenic anhydride which would correspond to the unsymmetrical chloride of phthalic anhydride.



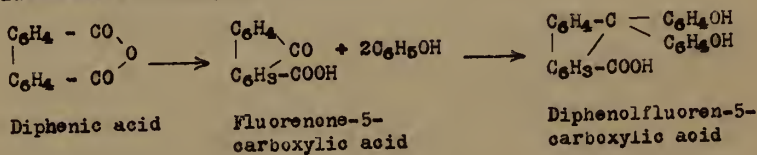
When diphenic anhydride and phosphorus pentachloride were heated in the proportion of one to one, it was found that the anhydride was partly converted into fluorenone-5-carboxylic acid. When the proportion was changed to one to two, and the melt was heated for two hours, a compound which gave a melting point of 124° was formed. The crystalline product was a golden colored powder which contained chlorine and which probably was the compound to which Graebe and Mensching assigned the formula $C_{28}H_{18}Cl_2O_5$, a dichloride of a double molecule of diphenic anhydride. Because of the fact that diphenic anhydride changes into the ketone acid upon heating with phosphorus pentachloride, the possibility of the formation of such a compound as the chloride of diphenic anhydride which would correspond to the unsymmetrical chloride of phthalic anhydride seems to be remote.

Condensation products of diphenic anhydride or rather of the fluorenone-5-carboxylic acid were next prepared with the idea in mind of comparing them with the condensation products of phthalic anhydride.

Preparation of Diphenolfluoren-5-carboxylic acid. Five grams of diphenic anhydride, four and two tenths grams of phenol, and four grams of sulphuric acid were mixed and heated to 120° for two hours. A light colored solution which was first obtained changed soon after the application of heat to a dark red. Upon turning the solution into water a precipitate came down which was filtered off and washed with water. This precipitate was dissolved in caustic soda and then thrown down again with hydrochloric acid. After this precipitate was filtered it was well washed and dried. It was a yellowish-pink powder, insoluble in water but soluble in alkalies, and alcohol. Upon being heated it

formed a dark viscous mass around 100°. Attempts to obtain crystalline salts ended in failure. A dilute solution in alcohol gave a pink coloration in alkalis and a colorless solution in acids. The indicator color was similar to that of phenolphthalein only very much weaker.

Five grams of diphenic anhydride were mixed with four and two tenths grams of phenol in an iron crucible placed in an oil bath. This mixture was heated to 140°, the temperature at which the diphenic anhydride went into solution. Then, ten grams of fused zinc chloride were stirred into the melt which immediately became brown in color. The temperature was raised to 180° and kept there for an hour and a half. The melt, which was stirred from time to time, became thicker and thicker until it was almost hard, whereupon the crucible was removed from the oil bath and allowed to cool. The fused mass was chipped from the crucible and boiled for a short time with acidulated water. The liquid was decanted from the resulting insoluble black mass, which was dissolved in sodium hydroxide and reprecipitated with very dilute hydrochloric acid. This precipitate was pinkish in color and, when filtered and dried, had the same physical characteristics as the compound given above. These characteristics agreed with those of the compound for which Graebe worked out the formula $C_{26}H_{18}O_4$ and which he claimed was a condensation product of fluorenone-5-carboxylic acid (1).

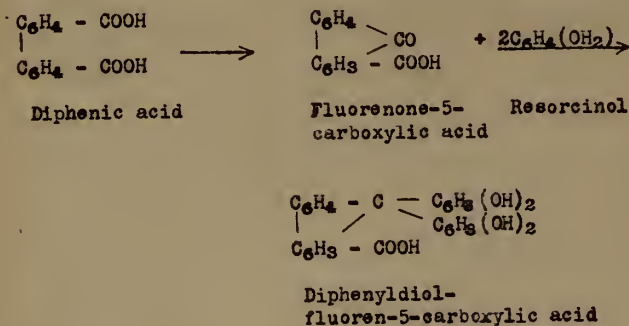


(1) Graebe and Aubin, Ann., 247:268

Preparation of Diphenyldiolfluoren-5-carboxylic acid.

A condensation product of diphenic anhydride and resorcinol was next formed. Fifteen grams of diphenic anhydride and fourteen and seven tenths grams of resorcinol were mixed in an iron crucible, placed in an oil bath and heated to 160° . At this temperature fusion occurred and thirty grams of fused zinc chloride were stirred into the liquid. The temperature of the bath was raised to 190° and kept there for one hour. During this time the fusion mass became reddish brown in appearance. The temperature of the mass was then raised to 215° , which was just below the temperature where the fusion mass appeared to boil. After maintaining this temperature for another hour, during which the mass became almost solid, the crucible was removed from the bath and cooled. Its contents were chipped out and boiled for a short time in water to which a little hydrochloric acid had been added. A black insoluble gummy mass which showed a beautiful greenish luster in reflected light formed in the bottom of the beaker. The zinc chloride solution was decanted and this black mass was washed well with water. It was then dissolved in sodium hydroxide and filtered to remove any zinc chloride that remained. Dilute hydrochloric acid was added to the filtrate until complete precipitation had occurred. This precipitate was light yellow in color, and after being filtered, it was washed with water until free from chlorides, and dried. The dry powder was brown in color, soluble in alkalis, alcohol, and ether, only slightly soluble in carbonates and water, and insoluble in benzene. In dilute solution in alcohol and alkalis it gave a pronounced greenish fluorescence^c to reflected or refracted light, while it showed a light yellow color to transmitted light.

This compound was the condensation product of two molecules of resorcinol and one molecule of fluorenone-5-carboxylic acid since diphenic anhydride is changed to the ketone acid by heating with zinc chloride.



A carbon hydrogen determination of this compound gave the following percentages:

	<u>Carbon</u>	<u>Hydrogen</u>
Percent calculated for $\text{C}_{26}\text{H}_{20}\text{O}_6$	73.24	4.23
Percent obtained	72.97	4.60

These percentages show definite agreement with the formula just given which Graebe assigned to this compound.

Diphenyldiolfluoren-5-carboxylic acid resembles fluorescein in several respects: like fluorescein it is a light-colored powder, it forms bromine and iodine derivatives, it shows a marked fluorescence in dilute alcohol and alkali solutions; it dyes silk a yellowish brown, its molecule, both in the manner of building, and in the completed structure, exhibits a very striking similarity.

It is stated in many references that the fluorescence of fluorescein is due to the presence of the pyrone grouping. Now when resorcinol

was heated on an oil bath with zinc chloride, a condensation of resorcinol took place in which water was eliminated. The exact result of this condensation was not worked out but the product obtained showed the same marked fluorescence in alkali and alcohol solution that both fluorescein and diphenyldiolfluoren-5-carboxylic acid did. Now, making the reasonable assumption that no reaction took place other than the elimination of water from two or more molecules of resorcinol it is obviously impossible to obtain any combination of resorcinol that will admit a pyrone grouping. And it is certain that the fluorescence of these three compounds fluorescein, diphenyldiolfluoren-5-carboxylic acid, and the condensed resorcinol molecules is due to the presence of similar groups, since neither phthalic anhydride nor fluorenone-5-carboxylic acid possesses any observable fluorescence by itself, while resorcinol when linked up alone by a process that is comparable to the manner in which it is linked up in the above-mentioned compounds, possesses a degree, and a kind of fluorescence that, to the eye, appears to be identical to the fluorescence that these former compounds show. Thus, the phenomena of fluorescence in these cases is not dependant upon the presence of a pyrone grouping, but, it is more likely due to the position and relation of the hydroxyl groups to the rest of the molecule, since, when the hydroxyls are replaced by chlorine the fluorescence completely disappears; moreover, when the influence of the hydroxyl is over-shadowed by the addition of adjacent atoms such as bromine, or iodine, the depth of the light phenomena is markedly decreased.

Preparation of Tetrabromodiphenyldiol-fluoren-5-carboxylic acid.

Five grams of diphenyldiolfluoren-5-carboxylic acid were dissolved in twenty

cubic centimeters of alcohol in a small Erlenmeyer flask. Three and four tenths cubic centimeters of bromine were slowly added to this solution from a long stemmed burette. A reaction took place in which considerable heat was evolved. The color of the solution changed from greenish yellow to a deep red. This solution was left standing for half a day in order to be sure that the reaction was complete. The contents of the flask were then turned into about one hundred cubic centimeters of water whereupon a heavy flocculent precipitate appeared which, after warming on the waterbath, coagulated and was easily filtered. The product smelt strongly of bromine, so it was dissolved in sodium hydroxide and reprecipitated by the addition of hydrochloric acid. After filtering again it was well washed with water and dried.

This compound was a red powder which was soluble in alkalis and alcohols with an intense red color, and which was insoluble in water, and acids. It did not show a definite crystalline form. It fused with partial decomposition around 180° .

A Carius determination of this red powder gave the following percentage of bromine: 43.21%.

It was thought possible that this bromine derivative might have come out of the alcohol solution with some molecules of alcohol of crystallization. Thus, the red powder was put on an air bath and heated to 120° for an hour, in order to expel any alcohol present. No change in form or color of the powder occurred, but when a Carius determination was made on it, a lower percentage of bromine was obtained than in the first case. The percent bromine was found to be 41.1% in this dried product.

If four atoms of bromine were substituted in one molecule of diphenyldiolfluoren-5-carboxylic acid, and if a molecule of alcohol of crystallization were present, the empirical formula $C_{26}H_{21}O_7Br_4$ would be satisfied by the percentage of bromine that was found in the first analysis of the red powder.

Percent bromine in the empirical formula $C_{26}H_{21}O_7Br_4$:

Percent bromine found = 43.21

Calculated = 43.1

In the second case, that is, in the analysis of product that resulted when the compound, the formula of which was just given, was heated to expel any possible alcohol, or water of crystallization, the percent bromine found did not agree with that, that there would be in tetrabromodiphenyldiolfluoren-5-carboxylic acid, but it did agree with the amount of bromine that there would be in the ethyl ester of tetrabromodiphenyldiolfluoren-5-carboxylic acid which has the empirical formula $C_{26}H_{19}O_6Br_4$.

Percent bromine in the empirical formula $C_{26}H_{19}O_6Br_4$:

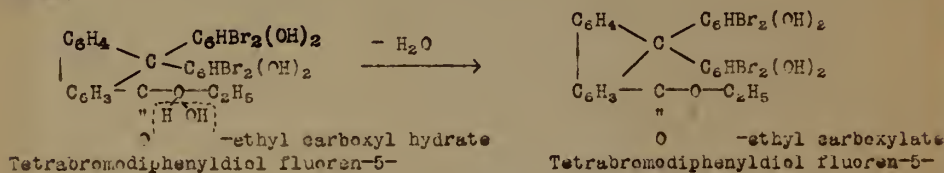
Percent bromine found = 41.1

Calculated = 41.5

By the correlation of the facts given above with the relationship that this compound showed to eocine it can be asserted that four bromine atoms were substituted in one molecule of diphenyldiolfluoren-5-carboxylic acid. The fact that one molecule of alcohol, per one molecule of tetrabromodiphenyldiolfluoren-5-carboxylic acid, was taken up as alcohol of

crystallization to form a compound which, on subsequent heating, gave up a molecule of water can be explained in two ways.

First, that the water which was produced in the formation of the ethyl ester of tetrabromodiphenyldiolfluoren-5-carboxylic acid became water of hydration, which upon heating was easily driven off. Second, the facts can be explained by means of the oxonium theory, i.e., that oxygen can become tetravalent. The alcohol could form an addition product as is shown below.



Water could easily split off leaving the ethyl ester of tetrabromodiphenyldiolfluoren-5-carboxylic acid. Now, in the experiment just described, the ethyl ester of diphenyldiolfluoren-5-carboxylic acid could easily be formed under the conditions that existed. When the free ketone acid was heated with alcohol in the presence of hydrochloric acid the ethyl ester of the ketone acid was formed. In the experiment in which the bromo derivative was formed, conditions existed that were similar to those, under which the ethyl ketone acid ester was made. The acid group was still unoccupied, the solute was alcohol, and the bromine would yield with the small amount of water present, the free acid that acts as a necessary agent in such an esterification. Thus, it is evident that the formation of the ethyl ester was favored by the conditions^{of} the experiment.

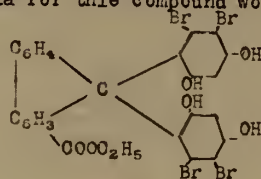
Preparation of the Sodium Salt of Tetrabromodiphenyldiolfluoren-5-ethyl carboxylate. Three grams of the bromo derivative were dissolved in five cubic centimeters of alcohol to which was then added a solution which consisted of one-half a gram of sodium carbonate in ten cubic centimeters of water. This mixture was heated on the waterbath until all ef-

fervescence had ceased. Fifteen cubic centimeters of alcohol were added to this mixture, in order to throw out of solution the sodium carbonate which is insoluble in alcohol, and the mixture was heated to boiling and filtered. The filtrate was allowed to evaporate and it produced a dark red powder which was completely soluble in water. This was the sodium salt of the bromine derivative.

Preparation of the Ammonium Salt of Tetrabromodiphenyldiolfluoren-5-ethyl carboxylate. The ammonium salt was formed, in the following manner. Three grams of the bromine derivative were spread out in a thin layer on a filter paper which was supported over a concentrated solution of ammonium hydroxide in an evaporating dish. Over this dish a large funnel was inverted thru the stem of which by means of a suction pump a stream of air was drawn. The red powder spread out on the filter paper changed to a purple color almost as soon as the first ammonia gas passed thru it. After a half hour a portion of the purplish powder was tested and found to be easily soluble in water without leaving a residue. This purplish powder was the ammonium salt of the bromine derivative which corresponded to the sodium salt.

The analogy that is shown between fluorescein and diphenyldiolfluoren-5-carboxylic acid is continued by the relationships that are evidenced in their tetrabromo derivatives, eosine and tetrabromodiphenyldiolfluoren-5-carboxylic acid. The bromo derivatives are red powders which have mutual solvents. In solution in the form of salts their color is very similar. In dilute alkali solution both compounds exhibit that delicate rose-pink fluorescence that gave to eosine its name signifying the dawn. Both form salts which are made in exactly the same way, and

which dye silk a rose-pink. Both take up a molecule of alcohol from an alcohol solution. The fundamental relationships in structure, that are observable in Fluorescein and diphenyldiolfluoren-5-carboxylic acid, are not changed by the addition of bromine to their molecules. It is not going too far to complete the analogy by affirming that the four bromine atoms occupy similar places in each bromine derivative. So the completed formula for this compound would be



Tetrabromodiphenyldiol
fluoren-5-ethyl carboxylate

Preparation of Diphenyltriol-fluoren-5-carboxylic Acid. A

condensation product of pyrogallol and diphenic anhydride was next prepared. Five grams of diphenic anhydride were heated with five and six-tenths grams of gallic acid in an iron crucible on an oil bath to 160°. At this point mutual evolution was complete and ten grams of fused zinc chloride were slowly stirred in. Carbon dioxide was evolved and the melt turned red. After the temperature of the bath had been raised to 210° and kept there for one hour and a half, the fusion mass became solid and was removed from the bath. Then the crucible was cooled and its contents were chipped out, thoroughly washed with water, dried, and powdered.

This product was a grayish powder which was soluble in alcohol and alkalis, slightly soluble in hot water, and insoluble in chloroform and acids. Its solution in alkalis and acids gave a very deep reddish-brown color.

It forms compounds with bromine that are not deeply colored. In this respect it fails to obey the general rule which phthaleins as a class follow, that as the molecular weight of the compound is increased the color increases in depth; that is from yellow thru red, violet, to green.

A carbon-hydrogen determination gave the following result: carbon = 71.06%, hydrogen = 3.32%. This compound from its manner of building, when judged as a condensation product of fluoranone-5-carboxylic acid, such as diphenyldiolfluoren-5-carboxylic acid and diphenolfluoren-5-carboxylic acid, should bear, structurally, the same relation to galleine as its lower phenol brothers bear to fluorescein, and phenolphthalein. A compound of the formula $C_{26}H_{18}O_8$ would show a theoretical carbon percentage equal to 68.12%, and a hydrogen percentage equal to 3.93%. These figures do not coincide with the percentages found, but they would agree fairly well if the molecule $C_{26}H_{18}O_8$ lost a molecule of water. These figures put together in table form are below:

	Carbon	Hydrogen
Calculated for:		
$C_{26}H_{18}O_8$	68.12	3.93
$C_{26}H_{16}O_7$	70.91	3.63
Percent found	71.06	3.32

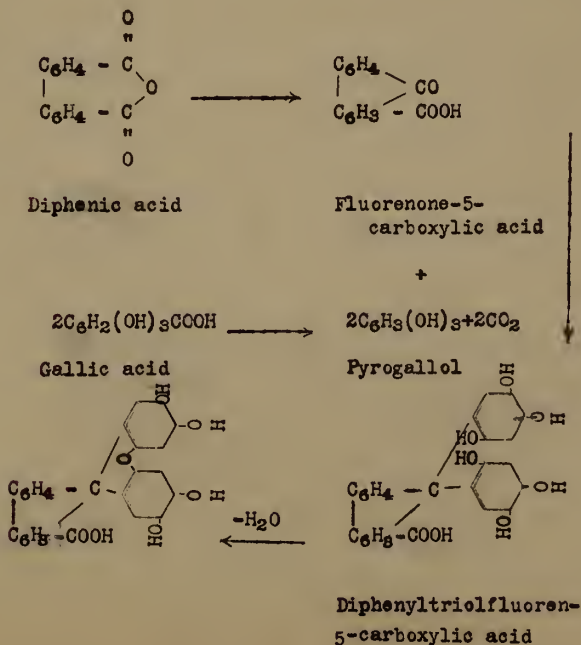
The figures from this ultimate analysis agreed with the results that were expected. The above-mentioned compound must therefore be a condensation product of fluorenone-5-carboxylic acid and pyrogallol since

the gallic acid was decomposed, on heating, to pyrogallol and carbon-dioxide.

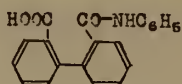
This compound loses a molecule of water in some way, during its formation. If two pyrogallol groups were condensed on one carbon atom, a hydroxyl group on each molecule would come in juxtaposition to another hydroxyl group.

On account of this proximity, during the course of the reaction in which this compound was formed, there would be a tendency, due to the presence of the dehydrating agent zinc chloride, towards the elimination of water from these two hydroxyl groups with the consequential linking up of the two benzene nuclei which would result in the formation of a pyrone ring.

The steps of the reactions of this experiment are given below:



Condensation Product of Aniline and Diphenic Anhydride. Diphenic acid anhydride and aniline when fused with zinc chloride in the same manner as in the preparation of those condensation products previously described, combined to form a compound which inasmuch as it contained no free amino groups was, without doubt, an acid anilide of either diphenic acid or of fluorenone-5-carboxylic acid.



Mono-anilide of diphenic acid.

This type of a reaction is characteristic of aniline which does not, as a rule, condense with anhydrides, as the phenols do, to form compounds like the phthaleins. This compound however was not considered to be of enough interest to be investigated.

Condensation Product of Hydroquinone and Diphenic Anhydride. Diphenic anhydride and hydroquinone, when fused with zinc chloride in the manner just referred to, united to form a compound which was not experimented with further. The fact, though, that a compound was formed may be found to be of interest in subsequent work if it can be proven that this compound is a condensation product similar to those already described of phenol and resorcinol. This possibility is, however, remote since such a condensation has not been known to occur when the para position to the substituted groups in the benzene ring has been occupied by any group other than a hydrogen or a halogen-like element. This compound was most probably an ester of hydroquinone with the carboxyl group of the ketone acid.

Preparation of Diphenyldimercaptofluoren-5-carboxylic acid.

Five grams (one molecule) of diphenyldiolfluoren-5-carboxylic acid were mixed with twelve grams (four molecules) of phosphorus pentachloride. The reaction, which began without the aid of heat, was completed by warming on the waterbath for an hour with considerable stirring. The black mass that resulted was extracted with benzene. The product that was obtained upon evaporation of the benzene was warmed on the waterbath with a concentrated solution of potassium hydroeulphide, into which a slow stream of hydrogen sulphide was conducted. After treating in this manner for an hour, the solution was turned into a beaker which contained water that was kept slightly acidulated with hydrochloric acid. A pinkish-colored voluminous precipitate came down which was freed from all traces of eulphides by dissolving in dilute sodium hydroxide and reprecipitating with hydrochloric acid. After washing free from chlorides and drying the precipitate appeared as a dark brown powder which was soluble in alkalis, sparsely soluble in alcohol and insoluble in ether, chloroform, and water.

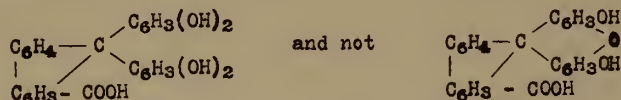
A Carius determination for sulphur gave a percent sulphur equal to 26.8%.

The experiment just detailed, was an attempt to replace the hydroxyl groups of diphenyldiolfluoren-5-carboxylic acid with mercaptan groups, thru the intermediate formation of the chloride compound. The percent sulphur obtained corresponded to the theoretical percentage of sulphur that there would be in a compound of diphenyldiolfluoren-5-carboxylic acid that contained four sulphur atoms.

calculated for $C_{26}H_{18}O_2S_4$ percent S = 26.8

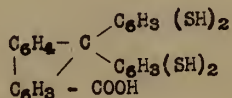
percent sulphur obtained = 26.2

The four sulphur atoms would be contained in four mercaptan groups because of the method of the experiment. Now it is highly probable that the four sulph-hydro groups replaced four hydroxyl groups and that there was no pyrone ring in the compound since the admission of four chlorine atoms into the compound thru phosphorus pentachloride was easily obtained. This entrance would probably not have occurred thru just warming on the waterbath if there had been a pyrone ring to enter into, since to replace that particular group in a compound usually requires considerable energy.



Several lines of evidence supported the probability of the existence of four hydroxyls. First, in the ultimate analysis of diphenyldiolfluoren-5-carboxylic acid a result was obtained which could be interpreted by the presence of four hydroxyl groups; second, in the Carius determination for bromine on tetrabromodiphenyldiolfluoren-5-ethylcarboxylate calculations agreed with a formula in which four hydroxyls were present; lastly, here in the replacement of hydroxyls by sulph-hydro groups, additional evidence as to the existence of four hydroxyls in diphenyldiolfluoren-5-carboxylic acid is furnished.

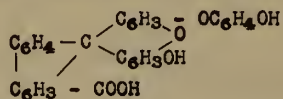
The formula, then, for the mercaptan derivative would be written in this manner:



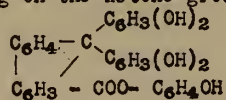
Diphenyldimercapto-fluoren-5-carboxylic acid.

Further Condensation of Resorcinol with Fluorenone-5-carboxylic acid.

The ease with which two or more molecules of resorcinol linked up with the elimination of water suggested the idea that perhaps more than two molecules of resorcinol might unite to form a condensation product with fluorenone-5-carboxylic acid in the following way:



There is also a possibility that resorcinol or a condensation product of resorcinol might form an ester with the acid group besides condensing on the ketone group.



The investigation of this problem was only started. When one molecule of diphenic anhydride was heated with three and four molecules of resorcinol condensation products were formed which took the physical form, in the first case, of a reddish powder, in the second, of a yellow powder. These compounds in solution possessed the same intense greenish fluorescence that was shown by diphenyldiolfluorene-5-carboxylic acid.

SUMMARY

At the beginning of this investigation phenanthrene, by a series of oxidations, became in turn, phenanthraquinone, and diphenic acid. The second phase of this transformation was exhaustively looked into. No less than seven different oxidations of phenanthraquinone to diphenic acid were performed; of this number, one method was original, and in two others introduction of modifications improved the processes.

From the anhydride of diphenic acid, fluorenone-5-carboxylic acid was formed, which served as a base in the preparation of condensation products, (a) with phenol, yielding diphenol-fluoren-5-carboxylic acid, (b) with resorcinol, yielding diphenyldiolfluoren-5-carboxylic acid, and (c) with pyrogallol, yielding diphenyltriolfluoren-5-carboxylic acid. The description of the properties of the first two compounds and the description of the third compound are given here for the first time. An attempt to build up a similar condensation product with aniline resulted in the formation of an acid anilide. Hydroquinone yielded by a like reaction with fluoranone-5-carboxylic acid a product that will bear further investigation. Diphenyldiolfluoren-5-carboxylic acid gave a bromine derivative, tetrabromodiphenyldiolfluoren-5-carboxylic acid, and a sulphur derivative, diphenyldimercaptofluoren-5-carboxylic acid both of which have not been described before.

Comparisons drawn between the phthaleins of phthalic anhydride and diphenic anhydride show that a remarkable similarity exists in their manner of building, completed structure, physical and chemical characteristics and in the fact that the relationship is continued in their derivatives.

Finally, the possibility that future work in building up condensation products of resorcinol will possess an interest which will bear upon the theory of the color of phthalein compounds, is suggested.

ACKNOWLEDGEMENTS.

Acknowledgements are due to Doctor Chamberlain under whose personal direction and supervision this work has been carried out; to Professor Serex for the interest, and helpful suggestions that he has so kindly given from time to time, and to the other members of the Department, Doctors Peters, Wellington and Lindsey for the interest that they have shown during the progress of the work.

